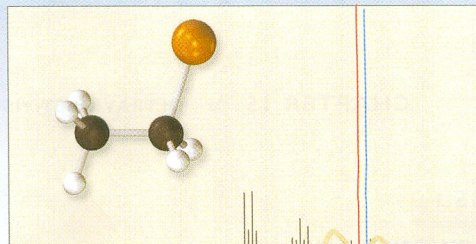


Ultraviolet-Visible Spectroscopy and Mass Spectrometry



CHAPTER

15

MASTERING ORGANIC CHEMISTRY

- ▶ Determining Whether a Compound Will Absorb Ultraviolet or Visible Light
- ▶ Identifying the Chromophore and Type of Transition Responsible for Absorption of UV Radiation
- ▶ Determining the Presence of Sulfur, Chlorine, Bromine, and Nitrogen from a Mass Spectrum
- ▶ Understanding the Major Fragmentation Pathways for Compounds Containing Some Simple Functional Groups

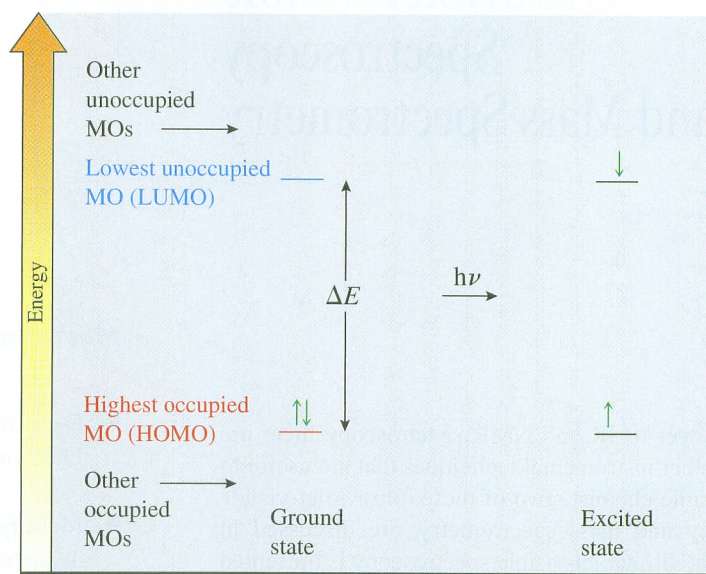
15.1 ULTRAVIOLET-VISIBLE SPECTROSCOPY

As discussed in Chapter 13, the ultraviolet (UV) region of the spectrum covers the range from 200 to 400 nm, and the visible region covers the range from 400 to 800 nm. The amount of energy available in this radiation, ranging from 143 kcal/mol (600 kJ/mol) to 36 kcal/mol (150 kJ/mol), is enough to cause an **electronic transition** in a molecule, that is, to excite an electron from an occupied MO to an antibonding MO.

Figure 15.1 shows a general diagram for such an electronic transition. The lowest-energy electron arrangement, the ground electronic state, is illustrated on the left side of the diagram. Only the highest-energy orbital that is occupied by electrons (the **highest occupied MO**, or **HOMO**) and the lowest-energy empty MO (**lowest unoccupied MO**, or **LUMO**) are shown in this diagram. In general, there are other occupied MOs at lower energies than the HOMO and other unoccupied MOs at higher energies than the LUMO (see Section 3.9). The HOMO

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Figure 15.1**GENERAL DIAGRAM FOR AN
ELECTRONIC TRANSITION.**

may be a bonding or a nonbonding MO; the LUMO is usually an antibonding MO. When the energy of the light matches the energy difference between the HOMO and the LUMO, the light is absorbed and an electron is promoted to the LUMO, producing the excited state. The electronic transition shown in Figure 15.1 is the lowest-energy one. Other transitions, resulting from the excitation of an electron from the HOMO to higher-energy unoccupied MOs or from the excitation of an electron from lower-energy occupied MOs to any of the unoccupied MOs, are also possible. Of course, all of these higher-energy transitions result in the absorption of shorter wavelengths of light.

Figure 15.2 shows the UV spectrum of 2,5-dimethyl-2,4-hexadiene. The wavelength of the light, in nanometers, is plotted along the x -axis, and the absorption band comes up from this axis, as was the case for NMR spectra. The wavelength range for most UV spectra begins at 200 nm because the O_2 of air and quartz glass absorb light with wavelengths shorter than this. Most absorption bands due to electronic transitions are broad and rather featureless like this one because each electronic energy level has numerous vibrational and rotational sublevels (see Figure 13.2).

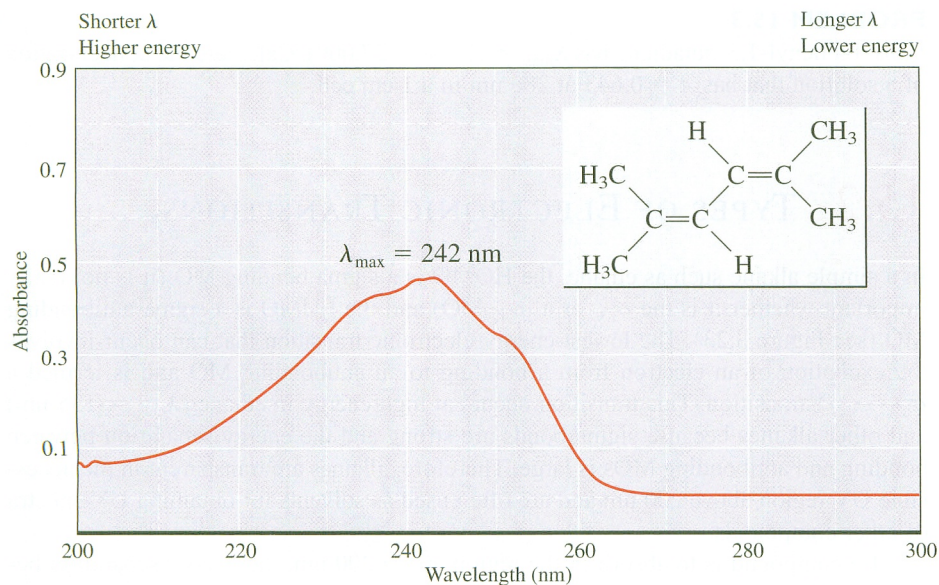
The amount of light absorbed by the sample is plotted along the y -axis as the **absorbance** (A), which is defined as

$$A = \log\left(\frac{I_0}{I}\right)$$

where I_0 is the intensity of the light striking the sample and I is the intensity of the light emerging from the sample. Absorbance is directly proportional to the concentration of the sample and the path length through the sample. The equation expressing this proportionality, known as the Lambert-Beer law, is

$$A = \epsilon cl$$

where ϵ is the **molar absorptivity** or the **molar extinction coefficient**, in units of $M^{-1} \text{ cm}^{-1}$, c is the concentration of the compound in moles per liter, and l is the path length

**Figure 15.2**

THE ULTRAVIOLET SPECTRUM
OF 2,5-DIMETHYL-
2,4-HEXADIENE.

in centimeters. (The Lambert-Beer law is very useful for quantitative analysis. You probably used this equation in the general chemistry laboratory to measure the concentration of a dissolved solute that absorbed UV or visible light.)

For a particular compound, the wavelength at the maximum of the absorption band (λ_{\max}) and the extinction coefficient at the maximum (ϵ_{\max}) are characteristic constants for that compound and are often listed in reference books along with the melting point, boiling point, and other physical constants of the compound. The solvent in which the sample is dissolved is also reported because λ_{\max} and ϵ_{\max} vary slightly with the solvent. 2,5-Dimethyl-2,4-hexadiene, whose UV spectrum is shown in Figure 15.2, has $\lambda_{\max} = 242$ nm and $\epsilon_{\max} = 13,100$ in methanol as solvent.

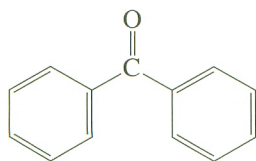
Although the λ_{\max} and ϵ_{\max} can be used like a melting point to aid in the identification of a compound, they also provide information about the energy separation between the MOs of the compound. Let's see how to use this to obtain information about the structure of the compound.

PROBLEM 15.1

Anthracene has $\epsilon = 1.80 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda_{\max} = 256$ nm. Calculate the absorbance of a $1.94 \times 10^{-6} \text{ M}$ solution of anthracene in a 1 cm cell.

PROBLEM 15.2

A solution of 0.0014 g of benzophenone in 1 L of ethanol has $A = 0.153$ (1 cm cell) at $\lambda_{\max} = 252$ nm. Calculate the molar absorptivity of benzophenone.



Benzophenone

PROBLEM 15.3

trans-1-Phenyl-1,3-butadiene has $\lambda_{\max} = 280$ ($\epsilon = 27,000$). Calculate the concentration of a solution that has $A = 0.643$ at 280 nm in a 1 cm cell.

15.2 TYPES OF ELECTRONIC TRANSITIONS

In a simple alkane such as ethane, the HOMO is a sigma bonding MO (it is not really important whether it is the σ_{CC} or a σ_{CH} MO) and the LUMO is a sigma antibonding MO (see Figure 3.23). The lowest-energy electronic transition that can occur involves the excitation of an electron from a bonding to an antibonding MO and is termed a $\sigma \longrightarrow \sigma^*$ transition. This transition occurs at high energy in ethane ($\lambda_{\max} = 135$ nm) and other alkanes because sigma bonds are strong and the energy separation between bonding and antibonding MOs is large. Therefore, alkanes are transparent in the accessible UV region above 200 nm and are often used as solvents for obtaining UV spectra of other compounds.

If a compound is to absorb in the region above 200 nm, the energy separation between its HOMO and LUMO must be smaller than in the case of alkanes. The bonding and antibonding MOs for pi bonds, which are weaker than sigma bonds, are closer together in energy (see Figure 3.24). Although the $\pi \longrightarrow \pi^*$ transition for ethene ($\lambda_{\max} = 165$ nm, $\epsilon_{\max} = 10,000$) still does not occur in the accessible UV region, it does occur at lower energy and longer wavelength than the $\sigma \longrightarrow \sigma^*$ transition of ethane.

Delocalized pi MOs must be used to describe compounds with conjugated pi bonds. This topic is covered in more detail in Chapters 16 and 22. For now it is enough to note that the energy of the highest bonding pi MO increases and the energy of the lowest antibonding pi MO decreases as the number of conjugated pi bonds in the compound increases. Figure 15.3 illustrates this for the series ethene, 1,3-butadiene, and 1,3,5-hexatriene. As would be expected based on this figure, λ_{\max} for the $\pi \longrightarrow \pi^*$ transition increases as the number of conjugated pi bonds increases and moves into the accessible UV region for dienes and trienes. As the **chromophore** (the part of the molecule that is responsible for the absorption of ultraviolet or visible light) becomes more conjugated, the absorption maximum moves to even longer wavelengths. Note also that the molar absorptivities for these $\pi \longrightarrow \pi^*$ transitions are all quite large.

In the case of an aldehyde or a ketone, the chromophore is the carbonyl group. The $\pi \longrightarrow \pi^*$ transition for acetone, like that for ethene, occurs below 200 nm ($\lambda_{\max} = 188$ nm) because there is no conjugation. However, acetone has electrons in nonbonding orbitals that are higher in energy than the pi electrons. The longest wavelength absorption for acetone is due to an $n \longrightarrow \pi^*$ transition ($\lambda_{\max} = 279$ nm, $\epsilon_{\max} = 15$). The molar absorptivity for the $n \longrightarrow \pi^*$ transition is much smaller than that for a typical $\pi \longrightarrow \pi^*$ transition because the n orbital and the π^* occupy different regions of space, resulting in a less probable transition.

Another chromophore that is commonly encountered in organic compounds is the benzene ring. Benzene itself has $\pi \longrightarrow \pi^*$ transitions with $\lambda_{\max} = 204$ nm ($\epsilon_{\max} = 7,900$) and 256 nm ($\epsilon_{\max} = 200$).

PROBLEM 15.4

Nitromethane has $\lambda_{\max} = 275$ nm ($\epsilon = 15$). What kind of transition is responsible for this absorption?

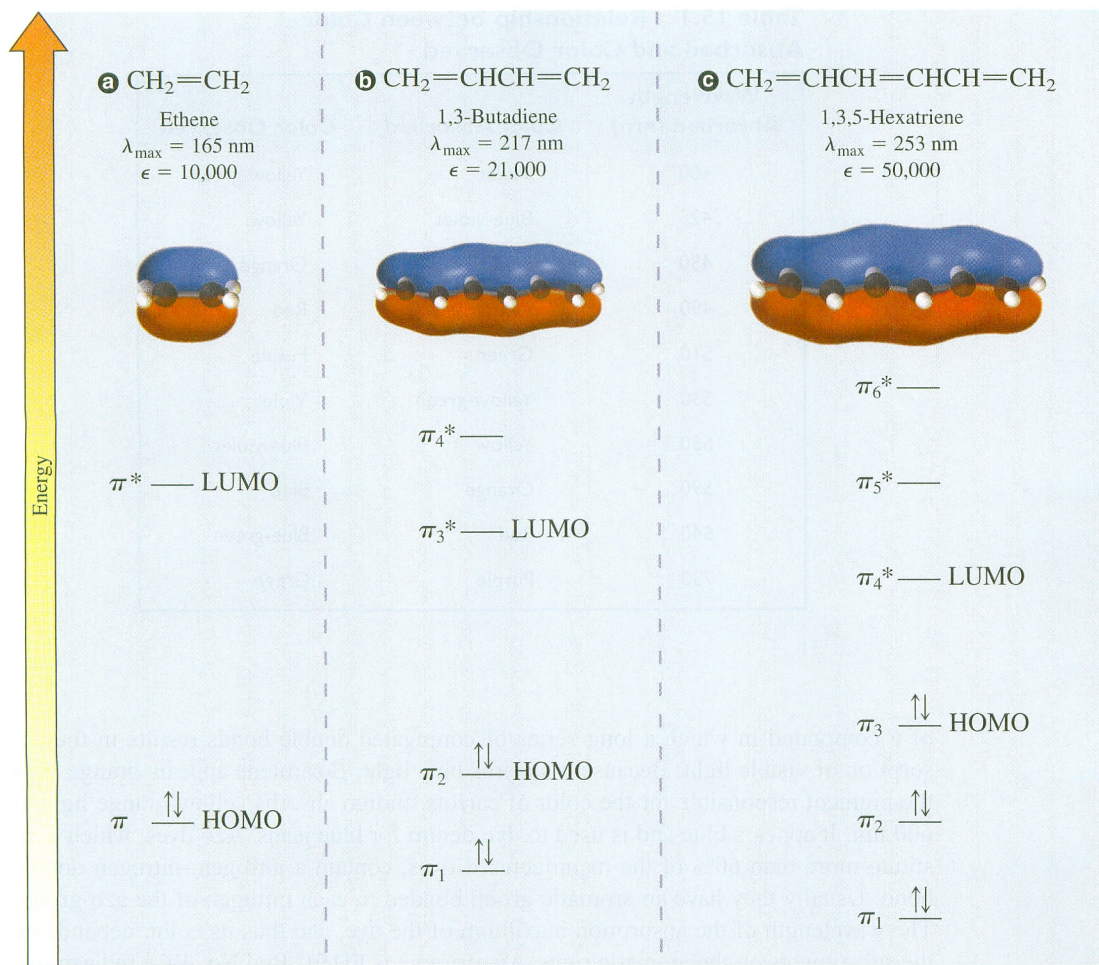


Figure 15.3

ENERGIES OF THE π MOs OF **a** ETHENE, **b** 1,3-BUTADIENE, AND **c** 1,3,5-HEXATRIENE.**PROBLEM 15.5**

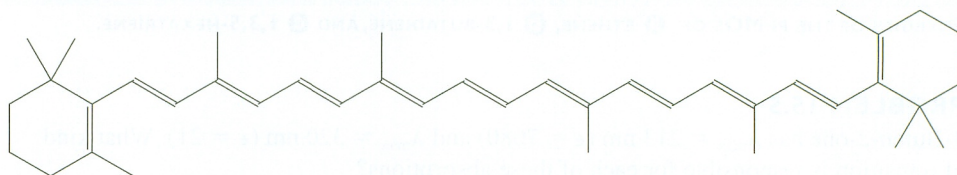
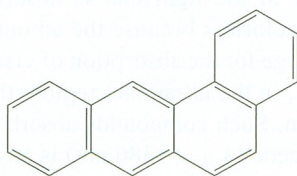
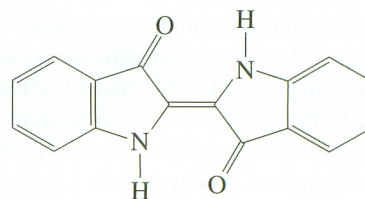
3-Buten-2-one has $\lambda_{\text{max}} = 213 \text{ nm}$ ($\epsilon = 7080$) and $\lambda_{\text{max}} = 320 \text{ nm}$ ($\epsilon = 21$). What kind of transition is responsible for each of these absorptions?

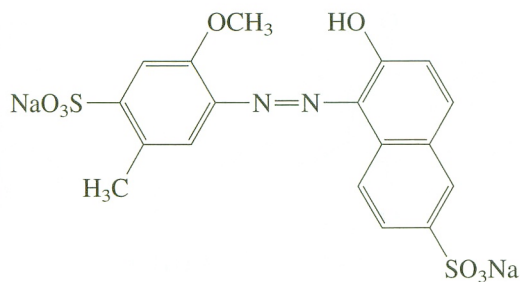
For a compound to be colored, it must absorb light in the visible region. The color of the compound is complementary to the color of the light that is absorbed (see Table 15.1). Most simple organic compounds are colorless because the amount of energy separating their HOMOs and LUMOs is too large for the absorption of visible light to occur. In the case of some compounds with λ_{max} in the ultraviolet region, the tail of the absorption band extends into the visible region. Such compounds absorb some of the violet light and appear yellow. 1,2-Benzanthracene ($\lambda_{\text{max}} = 386 \text{ nm}$) is an example of such a yellow compound. Compounds with even more extensive conjugation absorb visible light and appear colored. β -Carotene, which absorbs at 452 nm , is an example

Table 15.1 Relationship between Color Absorbed and Color Observed

Wavelength Absorbed (nm)	Color Absorbed	Color Observed
400	Violet	Yellow-green
425	Blue-violet	Yellow
450	Blue	Orange
490	Blue-green	Red
510	Green	Purple
530	Yellow-green	Violet
550	Yellow	Blue-violet
590	Orange	Blue
640	Red	Blue-green
730	Purple	Green

of a compound in which a long series of conjugated double bonds results in the absorption of visible light. Because it absorbs blue light, β -carotene appears orange. It is the pigment responsible for the color of carrots. Indigo absorbs yellow-orange light at 600 nm. It appears blue and is used to dye denim for blue jeans. Azo dyes, which constitute more than 60% of the manufactured dyes, contain a nitrogen–nitrogen double bond. Usually they have an aromatic group bonded to each nitrogen of the azo group. The wavelength of the absorption maximum of the dye, and thus its color, depends on the substituents on the aromatic rings. An example is FD&C Red No. 40, a red azo dye ($\lambda_{\text{max}} = 508 \text{ nm}$) that is used in food coloring.

 β -Carotene $\lambda_{\text{max}} = 452 \text{ nm}$ 1,2-Benzanthracene $\lambda_{\text{max}} = 386 \text{ nm}$ Indigo $\lambda_{\text{max}} = 600 \text{ nm}$

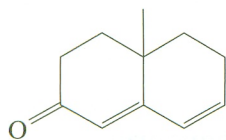


FD&C Red No. 40 (an azo dye)
 $\lambda_{\max} = 508 \text{ nm}$

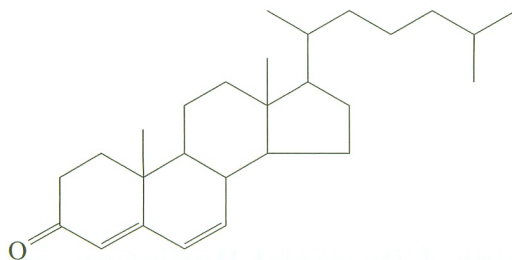
15.3 UV-VISIBLE SPECTROSCOPY IN STRUCTURE DETERMINATION

Although UV-visible spectroscopy is not as useful as IR or NMR, it does have value in structure determination because it provides information about the conjugated part of the compound. If a compound has no absorptions in the 200 to 800 nm region, then features such as conjugated carbon-carbon double bonds, carbonyl groups, and benzene rings must be absent. The presence of an absorption band usually does not allow, by itself, the identification of the responsible chromophore. However, the proposed chromophore must be consistent with the spectrum. The absorption maxima of a variety of compounds can be calculated with good accuracy by using several sets of empirical rules, so the UV spectrum can often be used to distinguish among isomeric chromophores.

In addition, structural features that are not directly attached to the chromophore have little effect on the spectrum. Therefore, smaller compounds that contain the same chromophore can be used as models to predict the spectra of larger compounds. As an example, the following two compounds have very similar UV spectra:

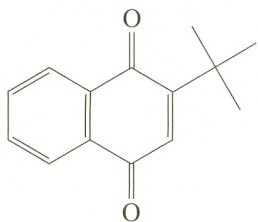
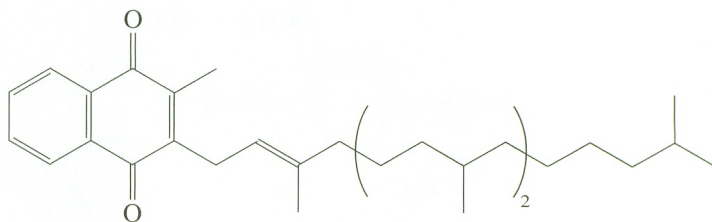


$\lambda_{\max} = 283 \text{ nm}$



$\lambda_{\max} = 284 \text{ nm}$

Studies using model compounds can be useful in structure determinations. For example, the presence of a 1,4-naphthoquinone chromophore in vitamin K₁ was suggested by the similarity of its UV spectrum to those of simpler compounds such as 2-*tert*-butyl-1,4-naphthoquinone:

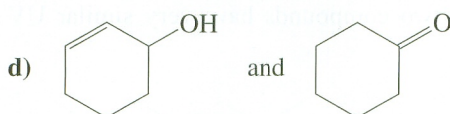
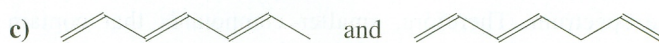
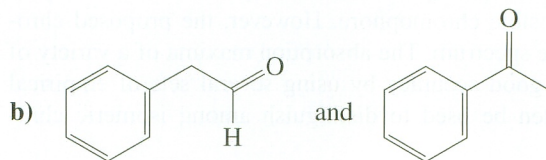
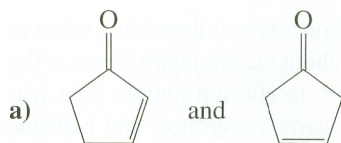
2-*tert*-Butyl-1,4-naphthoquinoneVitamin K₁

λ_{\max} (nm)	ϵ
249	19,600
260	18,000
325	2,400

λ_{\max} (nm)	ϵ
248	18,600
264	14,200
331	2,730

PROBLEM 15.6

Explain how UV spectroscopy could be used to distinguish between these compounds.



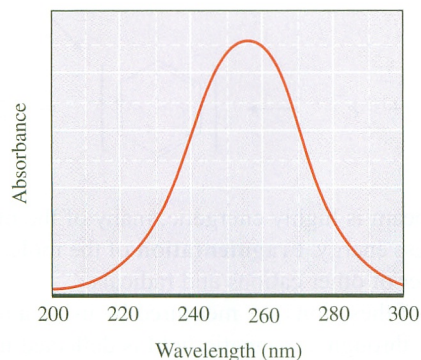
Focus On

Ozone, Ultraviolet Radiation, and Sunscreens

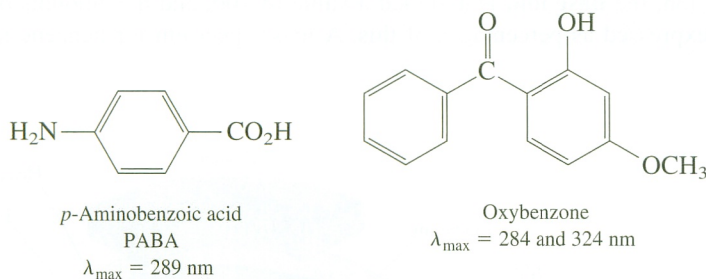
Ozone is an extremely reactive chemical. Its reaction with alkenes was discussed in Section 11.11. Although it is considered a pollutant in the lower atmosphere, its presence in the upper atmosphere has beneficial health effects due to its absorption of ultraviolet light.

The UV spectrum of ozone is shown in the following figure. There is enough ozone in the upper atmosphere that essentially all of the ultraviolet radiation of wavelengths less than 295 nm is absorbed. The tail of the ozone band absorbs part of the light in the

region from 295 to 320 nm. This radiation, known as UV-B, is responsible for sunburn and also causes damage to DNA that may result in skin cancer. Any decrease in the ozone concentration in the upper atmosphere allows more of this damaging UV-B radiation to reach the surface of the earth. This is why there is so much concern about the release of ozone-destroying chemicals, such as chlorofluorocarbons.



One way to protect against the damaging effects of UV-B radiation is to use a sunscreen. The active ingredient in a sunscreen is a compound that absorbs harmful ultraviolet radiation. Early sunscreens contained *p*-aminobenzoic acid, PABA, which has $\lambda_{\text{max}} = 289$ nm and absorbs strongly in the UV-B region. Newer formulations contain ingredients such as oxybenzone, which has $\lambda_{\text{max}} = 284$ and 324 nm. These current sunscreens are designed to absorb UV-A (wavelengths of 320–400 nm) in addition to UV-B radiation. Although it does not cause much burning, UV-A is thought to cause wrinkling and premature aging of the skin over long periods of exposure.

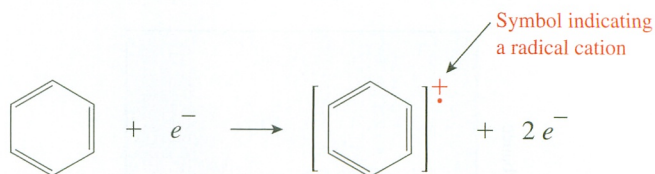


15.4 MASS SPECTROMETRY

Mass spectrometry is used to measure the molecular mass of a compound and provides a method to obtain the molecular formula. It differs from the other instrumental techniques presented thus far because it does not involve the interaction of electromagnetic radiation with the compound. Instead, molecules of the compound being studied are bombarded with a high-energy beam of electrons in the vapor phase. When an electron from the beam impacts on a molecule of the sample, it knocks an electron out of the molecule. The product, called the **molecular ion** (represented as M^+), has the same mass as the original molecule but has one less electron. It has both an odd number of



electrons and a positive charge. Species that have an odd number of electrons are called **radicals** (see Chapter 21). Therefore, the molecular ion is a **radical cation**. This process is illustrated in the following equation for the formation of the radical cation from benzene:



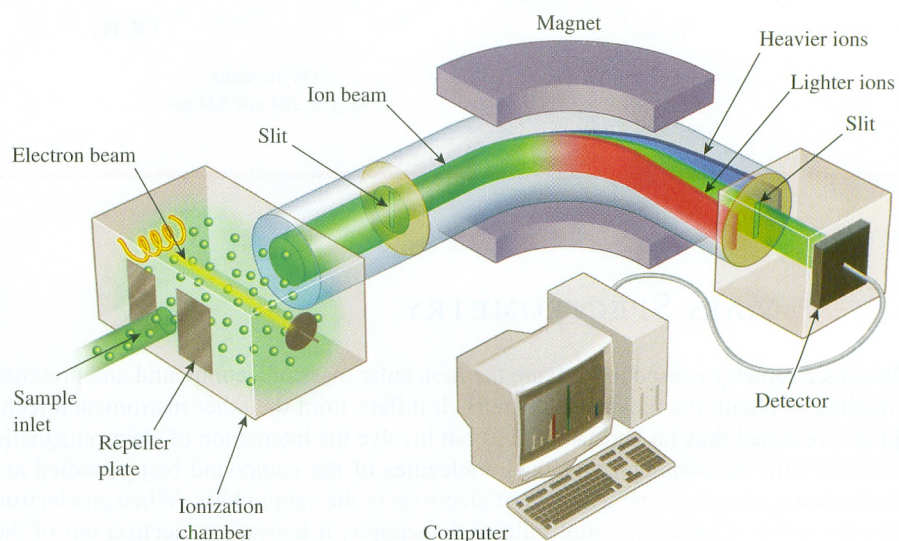
Because the electron beam is highly energetic, many of the molecular ions are formed with considerable excess energy. **Fragmentation** of the molecular ions with excess energy produces a number of other cations and radicals.

The masses of all of these ions are measured by using a magnetic field. A charged particle that is moving through a magnetic field is deflected in a direction perpendicular to the field. The amount of this deflection depends on the ratio of the charge to the mass of the ion. Heavier ions are deflected less than lighter ions. In a mass spectrometer, the **mass to charge ratio** (m/z) is measured. The charge on almost all of the ions is +1, so their masses can be determined. The mass of the molecular ion provides the molecular mass of the compound, whereas the masses of the fragment ions provide information about its structure. A schematic diagram of a mass spectrometer is shown in Figure 15.4.

The mass spectrum is a report of the relative numbers or abundances of ions of each m/z that are detected, and it is often presented in the form of a bar graph. The most abundant ion, the **base ion**, is assigned a value of 100, and the amounts of the other ions are expressed as percentages of this. A mass spectrum for benzene is shown in

Figure 15.4

SCHEMATIC DIAGRAM OF A MASS SPECTROMETER. In the ionization chamber, electron bombardment is used to eject electrons from sample molecules, creating radical cations. These are accelerated away from the positively charged repeller plate. A beam of these ions is passed into the magnetic field, which is perpendicular to the plane of the page. As the magnetic field strength is varied, ions of different mass to charge ratio pass through the slit and reach the detector. The data are sent to a computer, which records the relative numbers of ions of each mass.



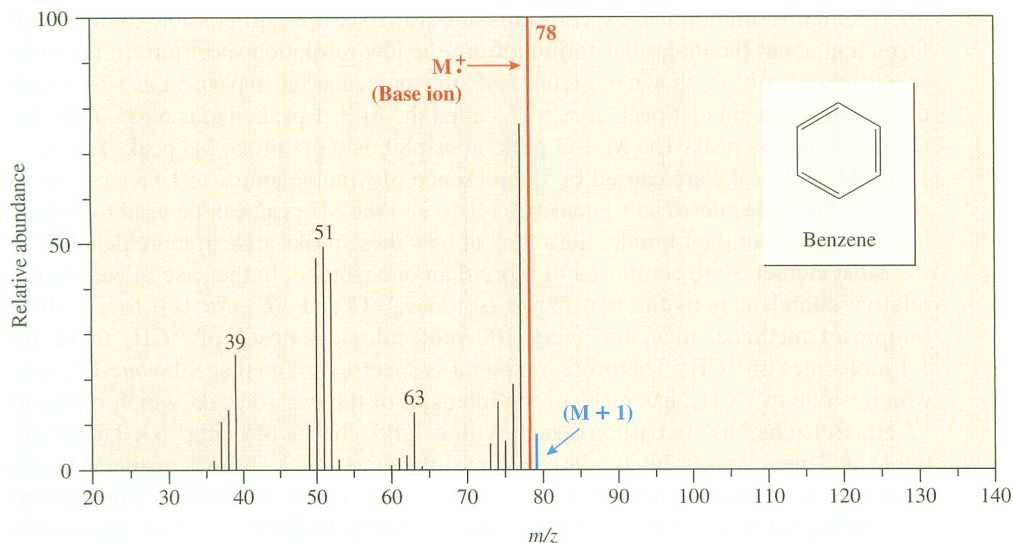


Figure 15.5

THE MASS SPECTRUM OF BENZENE.

Figure 15.5. In this particular case the molecular ion, at m/z 78, is also the base ion. More commonly, the base ion and the molecular ion are not the same.

15.5 DETERMINING THE MOLECULAR FORMULA

Two general types of mass spectrometers are available. The most common type, a low-resolution mass spectrometer, provides the masses of the ions to the nearest whole number. A more expensive instrument, a high-resolution mass spectrometer, provides the masses to several decimal places. The more accurate mass provided by a high-resolution instrument is especially useful in determining the molecular formula of the compound because the atomic masses of the various atoms are not exact integers. Consider the compounds CO_2 , $\text{C}_2\text{H}_4\text{O}$, and C_3H_8 . On a low-resolution mass spectrometer, these compounds all have a molecular ion at m/z 44. However, the exact masses of these compounds are all slightly different. Table 15.2 provides the exact masses of the major isotopes of a few elements that commonly occur in organic compounds. The exact mass of a CO_2 molecule is 43.9898, that of $\text{C}_2\text{H}_4\text{O}$ is 44.0262, and that of C_3H_8 is 44.0626. These masses can be readily distinguished with a high-resolution instrument.

PROBLEM 15.7

Butane and acetone both have a molecular mass of 58. Calculate the exact masses of these compounds and explain whether they can be distinguished by high-resolution mass spectrometry.

Table 15.2 Exact Masses of Some Common Isotopes

Isotope	Atomic Mass (amu)
^1H	1.00783
^{12}C	12.00000
^{14}N	14.0031
^{16}O	15.9949

These values are not the same as the atomic masses in the periodic table because these are the exact masses of individual isotopes. The masses in the periodic table are average masses of the element based on the masses and natural abundances of the isotopes of which it is composed.

If a high-resolution mass spectrum is not available, it is still possible to obtain information about the molecular formula from the low-resolution spectrum. In the mass spectrum of benzene, shown in Figure 15.5, the molecular ion appears at m/z 78. In addition, there is a smaller peak at m/z 79, called the $M + 1$ peak, that is 6.8% of the intensity of the M^+ peak. The $M + 2$ peak, at m/z 80, is 0.2% of the M^+ peak. The $M + 1$ and $M + 2$ peaks are caused by the presence of isotopic atoms of heavier mass in some of the molecules. Their intensities relative to the M^+ peak can be used to deduce information about the formula. Let's look at how these peaks arise in more detail.

Most elements are composed of more than one isotope. In the case of carbon the relative abundances of the two major isotopes, ^{12}C and ^{13}C , are 100 to 1.1. In a sample of methane, then, for every 100 molecules composed of $^{12}\text{CH}_4$ there are 1.1 molecules of $^{13}\text{CH}_4$. Therefore, in the mass spectrum of methane the m/z 17 peak, which is due to $^{13}\text{CH}_4$, has 1.1% of the intensity of the m/z 16 peak, which is due to $^{12}\text{CH}_4$. Benzene has six carbons, each with a 1.1% chance of being ^{13}C . Therefore, the $M + 1$ peak at m/z 79 should be approximately $6 \times 1.1 = 6.6\%$ of the M^+ peak at 78 m/z , in good agreement with the observed value of 6.8%. The $M + 2$ peak, with 0.2% of the intensity of the M^+ peak, is due primarily to molecules that contain two atoms of ^{13}C .

PROBLEM 15.8

What are the predicted intensities of the $M + 1$ peaks in the mass spectra of butane and acetone, relative to the intensity of the M^+ peak? Do you think that these intensities could be used to distinguish between these compounds?

Table 15.3 lists the relative abundances of the major isotopes of the elements that are commonly encountered in organic compounds. In principle, it is possible to use the

Table 15.3 Natural Abundances of Isotopes of Some Common Elements

Element	Major Isotope	RA	$M + 1$ Isotope	RA	$M + 2$ Isotope	RA
Hydrogen	^1H	100				
Carbon	^{12}C	100	^{13}C	1.1		
Nitrogen	^{14}N	100	^{15}N	0.4		
Oxygen	^{16}O	100			^{18}O	0.2
Fluorine	^{19}F	100				
Sulfur	^{32}S	100	^{33}S	0.8	^{34}S	4.4
Chlorine	^{35}Cl	100			^{37}Cl	32.5
Bromine	^{79}Br	100			^{81}Br	98.0
Iodine	^{127}I	100				

The relative abundance (RA) of the most abundant isotope is listed as 100, and the abundances of the other isotopes are listed relative to that number. The $M + 1$ isotope is the one that is responsible for the peak at m/z one unit higher than the peak for M^+ .

information in this table to determine the molecular formula of a compound on the basis of the intensities of its $M + 1$ and $M + 2$ peaks. In practice, this is difficult because of various inaccuracies that arise in measuring these intensities. Nevertheless, the presence of certain elements in a compound can readily be inferred from the size of the $M + 2$ peak:

The presence of one sulfur in the formula is indicated by an $M + 2$ peak that is about 4% of the M^+ peak.

The presence of one chlorine in the formula is indicated by an $M + 2$ peak that is about one-third as large as the M^+ peak (see Figure 15.6).

The presence of one bromine in the formula is indicated by an $M + 2$ peak that is about the same intensity as the M^+ peak (see Figure 15.7).

The presence of two of these atoms in the molecule results in the appearance of a characteristic pattern in the M^+ , $M + 2$, and new $M + 4$ peak, whereas the presence of three results in a different pattern, including an $M + 6$ peak.

The presence of one nitrogen in the formula is readily apparent because the molecular ion has an odd mass. To help understand why this is so, recall the degree of unsaturation calculation discussed in Section 2.4. Compounds consisting of carbon (even mass) and oxygen (even mass) have an even number of hydrogens and thus have M^+ at an even m/z . If a hydrogen (odd mass) is replaced by a halogen (odd mass), M^+ is still even. The presence of a single nitrogen (even mass) in a compound requires one additional hydrogen be present also. Because the total number of hydrogens is now odd, the molecular ion occurs at an odd m/z . In general, the appearance of the

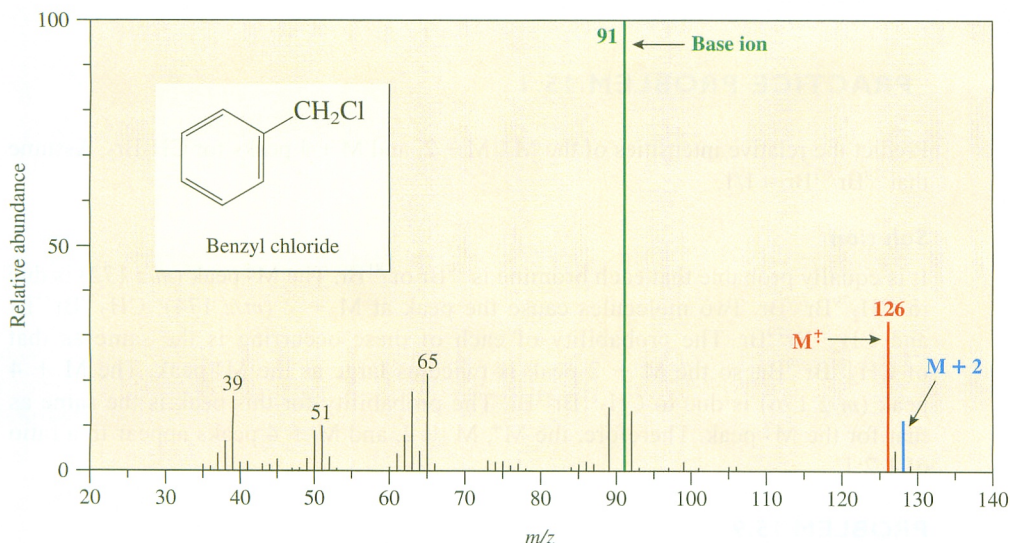


Figure 15.6

THE MASS SPECTRUM OF BENZYL CHLORIDE.

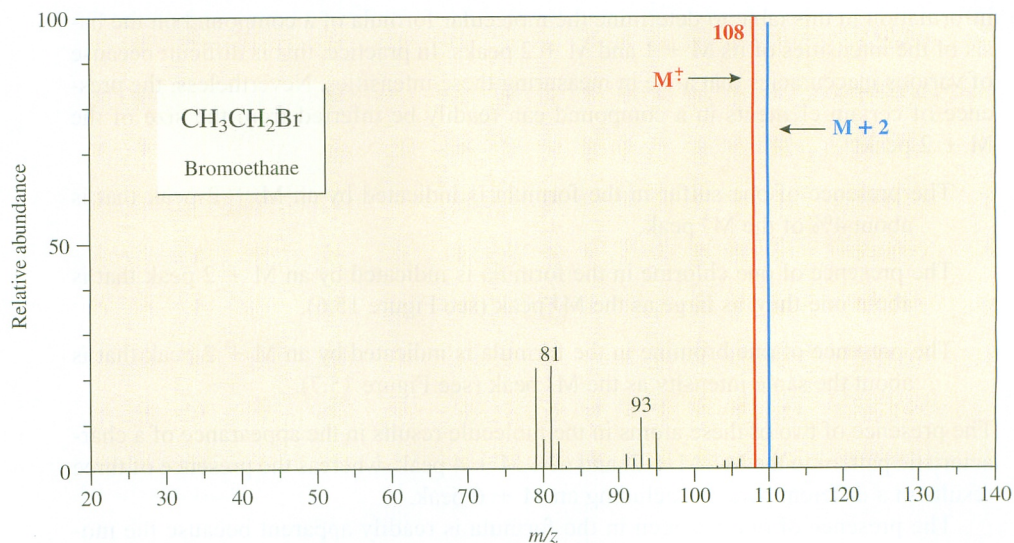


Figure 15.7

THE MASS SPECTRUM OF BROMOETHANE.

molecular ion at an odd m/z indicates the presence of an odd number of nitrogens in the formula.

PRACTICE PROBLEM 15.1

Predict the relative intensities of the M^+ , $M + 2$, and $M + 4$ peaks for CH_2Br_2 . Assume that $^{79}\text{Br}/^{81}\text{Br} = 1/1$.

Solution

It is equally probable that each bromine is ^{79}Br or ^{81}Br . The M^+ peak (m/z 172) is due to $\text{CH}_2^{79}\text{Br}^{79}\text{Br}$. Two molecules cause the peak at $M + 2$ (m/z 174): $\text{CH}_2^{79}\text{Br}^{81}\text{Br}$ and $\text{CH}_2^{81}\text{Br}^{79}\text{Br}$. The probability of each of these occurring is the same as that of $\text{CH}_2^{79}\text{Br}^{79}\text{Br}$, so the $M + 2$ peak is twice as large as the M^+ peak. The $M + 4$ peak (m/z 176) is due to $\text{CH}_2^{81}\text{Br}^{81}\text{Br}$. The probability for this peak is the same as that for the M^+ peak. Therefore, the M^+ , $M + 2$, and $M + 4$ peaks appear in a ratio of 1:2:1.

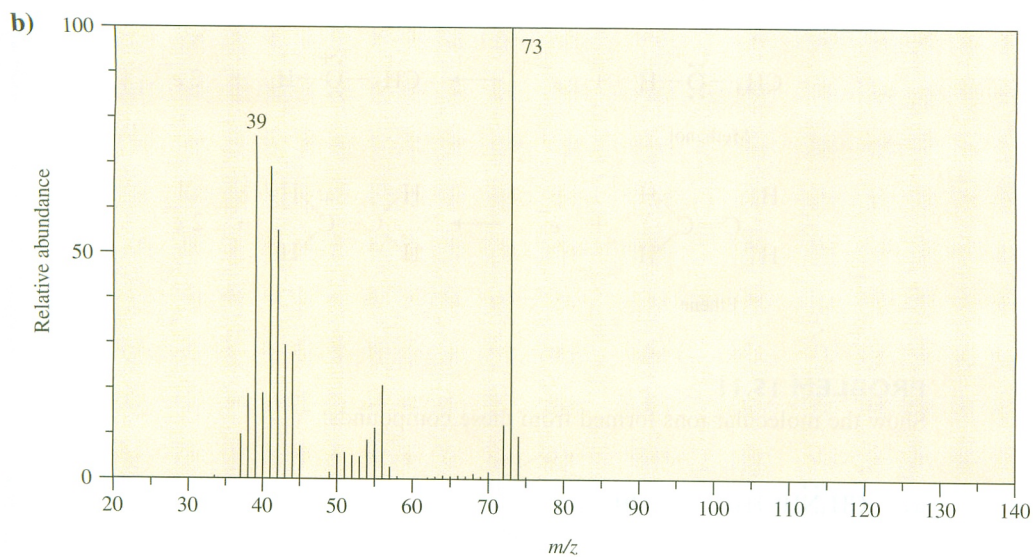
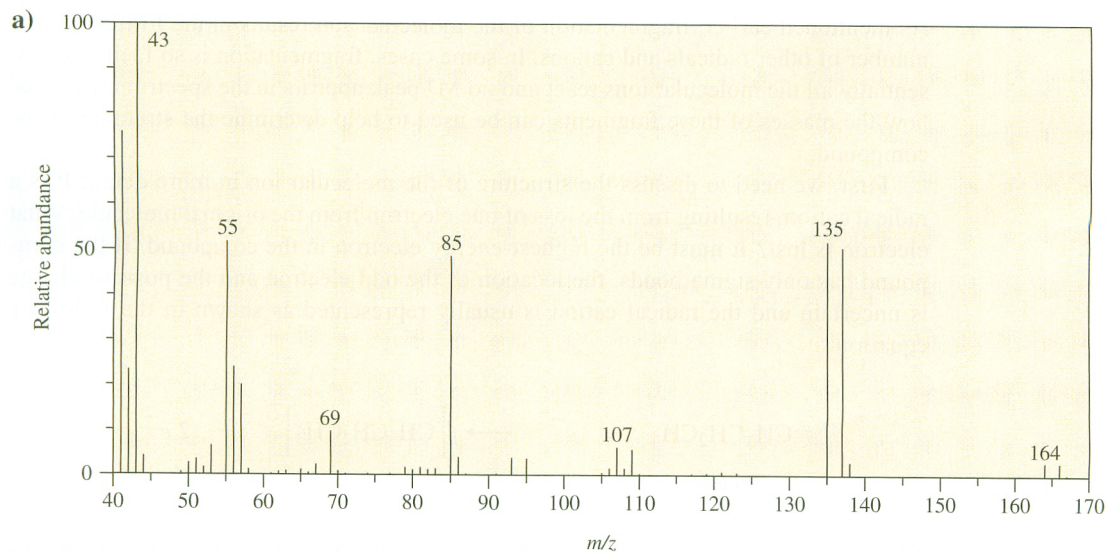
PROBLEM 15.9

Predict the relative intensities of the M^+ , $M + 2$, and $M + 4$ peaks for these compounds. Assume that $^{79}\text{Br}/^{81}\text{Br} = 1/1$ and $^{35}\text{Cl}/^{37}\text{Cl} = 3/1$.

- a) CH_2Cl_2 b) CH_2BrCl

PROBLEM 15.10

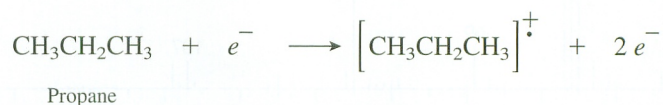
What conclusions can be drawn about these compounds from their mass spectra?



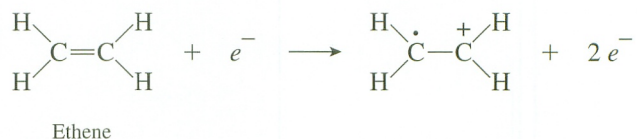
15.6 FRAGMENTATION OF THE MOLECULAR ION

As mentioned earlier, fragmentation of the molecular ion results in the formation of a number of other radicals and cations. In some cases, fragmentation is so facile that essentially all the molecular ions react and no M^+ peak appears in the spectrum. Let's see how the masses of these fragments can be used to help determine the structure of the compound.

First, we need to discuss the structure of the molecular ion in more detail. It is a radical cation, resulting from the loss of one electron from the original molecule. What electron is lost? It must be the highest-energy electron in the compound. If the compound has only sigma bonds, the location of the odd electron and the positive charge is uncertain and the radical cation is usually represented as shown in the following equation:

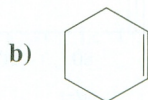


The radical cation from compounds that have nonbonding or pi electrons can also be represented in this manner. However, because the highest-energy electron is known in these cases, the structure of the radical cation can be drawn more specifically as illustrated in the following equations:



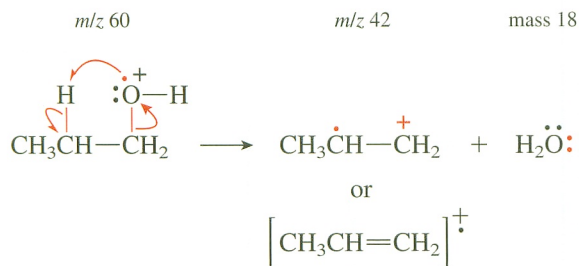
PROBLEM 15.11

Show the molecular ions formed from these compounds:



There are two general types of fragmentation reactions. In one type the radical cation fragments to a neutral molecule and a new radical cation. This process is especially favorable when the neutral product is a small, stable molecule. For example, the loss of water from the molecular ion of alcohols is very facile. For this reason the M^+ peak is very small for primary and secondary alcohols, and it is usually undetectable for

tertiary alcohols. An example of this fragmentation process is provided in the following equation. *Note the use of arrows with only half of the arrowhead to indicate movement of one electron rather than two.*

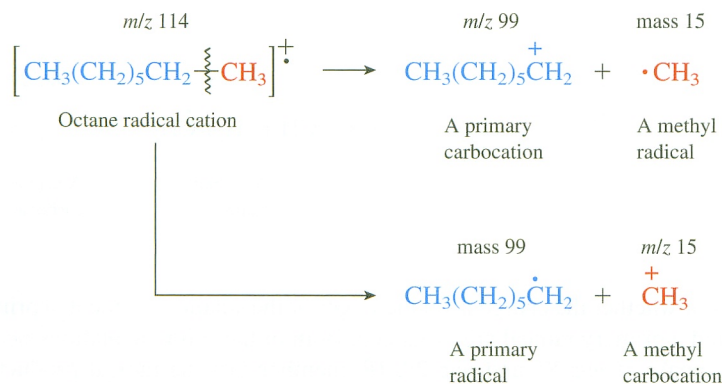


In the other type of fragmentation, a bond is cleaved so that the positive charge remains with one fragment and the odd electron goes with the other. Only the positive fragment is detected and appears in the mass spectrum. The stability of the product cation and radical determine the favorableness of this type of cleavage. You are already quite familiar with the factors that affect the stability of cations, especially carbocations. Although radicals are inherently more stable than carbocations because they are less electron deficient, they are stabilized by the same factors that stabilize carbocations. Thus, tertiary radicals are more stable than secondary radicals, and secondary radicals are more stable than primary radicals. Resonance stabilization is also important.

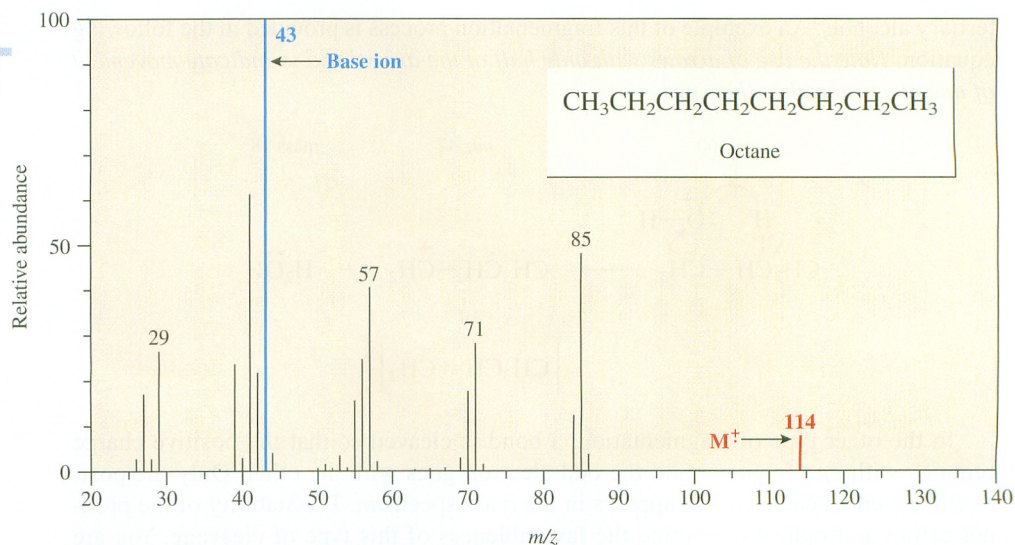
Let's see how these stabilities help to explain the fragmentations in some simple examples.

Alkanes

The mass spectrum of octane is shown in Figure 15.8. The molecular ion appears at m/z 114. Cleavage of the sigma bond between C-1 and C-2 would lead to the fragments shown in the following equations:

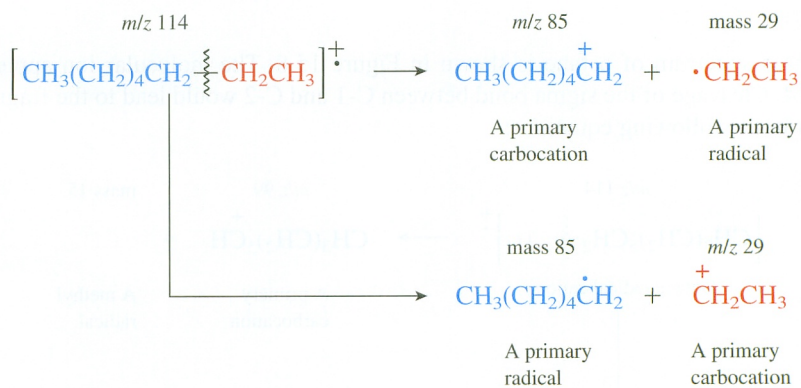


If the charge stays with the larger fragment, a primary carbocation, m/z 99 ($M - 15$), and a methyl radical are formed. This fragmentation is not favorable because the methyl radical is not very stable, so no peak at m/z 99 is observed in the spectrum. The process

Figure 15.8**THE MASS SPECTRUM OF OCTANE.**

in which the charge is on the smaller fragment produces a highly unstable methyl carbocation and is even less favorable.

Cleavage of the sigma bond between C-2 and C-3 leads to the fragments shown in the following equations:



Regardless of whether the charge is on the larger or the smaller fragment, a primary carbocation and a primary radical are produced. Both of these fragmentations occur as indicated by peaks at m/z 85 and m/z 29. (Remember that the radical products do not appear in the spectrum; only the cations are detected.) A similar cleavage between C-3 and C-4 results in peaks at m/z 71 and 43, whereas one between C-4 and C-5 gives a peak at m/z 57. The series of peaks separated by 14 units, the mass of the CH_2 fragment, is characteristic of straight-chain alkanes.

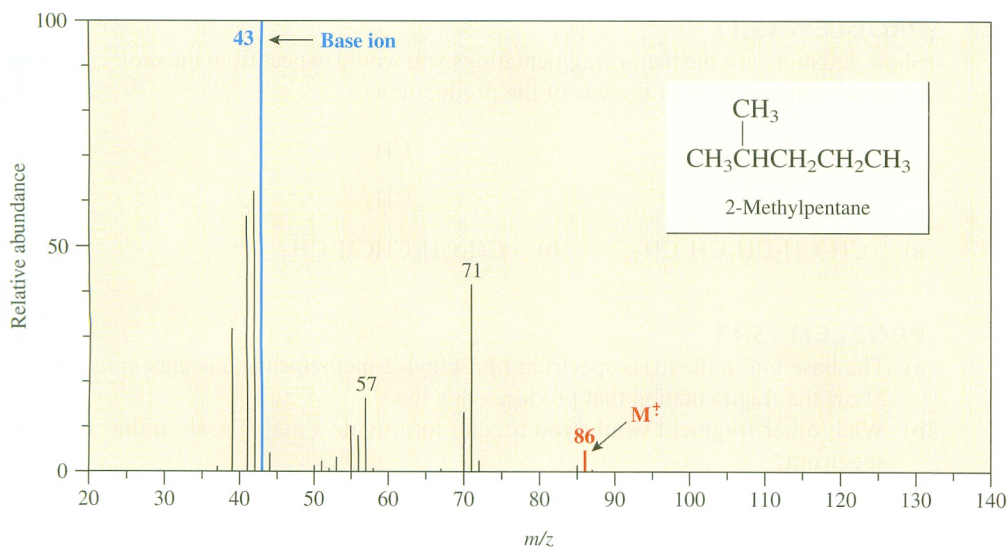
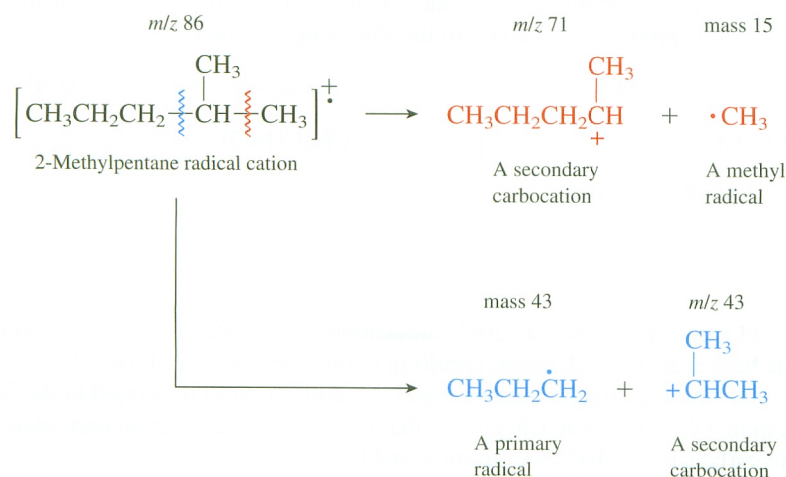


Figure 15.9

THE MASS SPECTRUM OF
2-METHYLPENTANE.

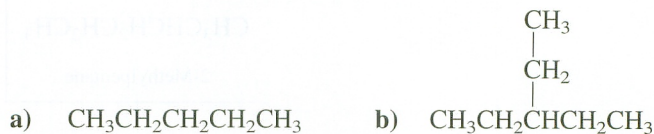
Figure 15.9 shows the mass spectrum of 2-methylpentane. Branched alkanes tend to cleave on either side of the branch because more stable carbocations result. The two primary cleavage pathways for 2-methylpentane are shown in the following equations:



Although the fragmentation required to produce a methyl radical and a primary carbocation did not occur in the case of octane, the loss of a methyl radical does occur here because the resulting carbocation, with m/z 71, is secondary. Cleavage on the other side of the branch results in the formation of a primary radical and a secondary carbocation, with m/z 43. This is the most favorable fragmentation, so m/z 43 is the base ion.

PROBLEM 15.12

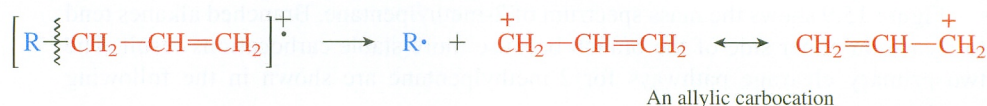
Show equations for the major fragmentations you would expect from the molecular ions of these compounds. List the m/z of the product ions.

**PROBLEM 15.13**

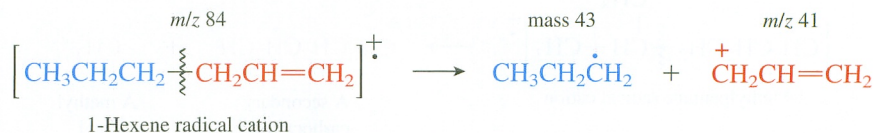
- a) The base ion in the mass spectrum of 3-ethyl-2-methylpentane occurs at m/z 43. Show the fragmentation that produces this ion.
 b) What other fragment would you predict to provide a major peak in the spectrum?

Alkenes

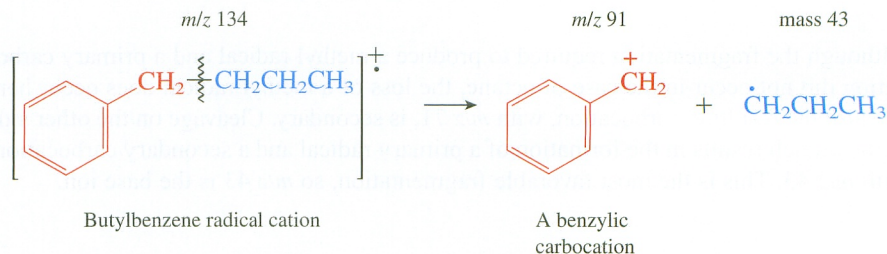
The fragmentation of an alkene to produce an allylic carbocation is usually a major pathway because of resonance stabilization:



The base ion in the spectrum of 1-hexene, Figure 15.10, is the allylic carbocation with m/z 41, which is produced according to the following equation:

**Benzylic Cleavage**

The benzyl carbocation, like the allyl carbocation, has substantial resonance stabilization. The base peak at m/z 91 in the spectrum of butylbenzene (see Figure 15.11) results from a fragmentation that produces a benzylic carbocation as illustrated in the following equation. (We will see in Chapter 16 that the benzylic carbocation rearranges to an isomeric carbocation, which is even more stable.)



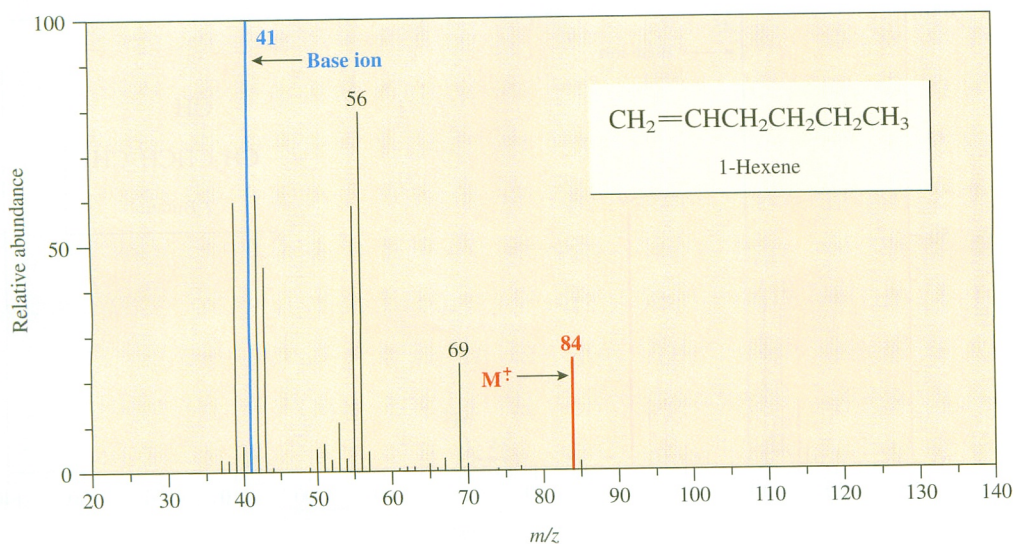


Figure 15.10

THE MASS SPECTRUM OF 1-HEXENE. Note that many of the peaks in this spectrum and others are difficult to explain. This is because of rearrangements and other fragmentations that we have not discussed.

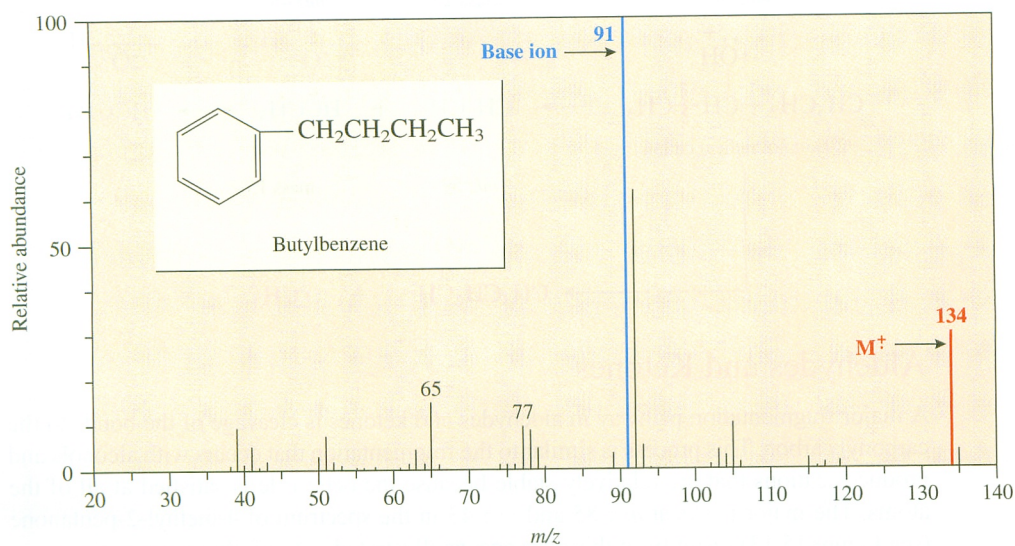


Figure 15.11

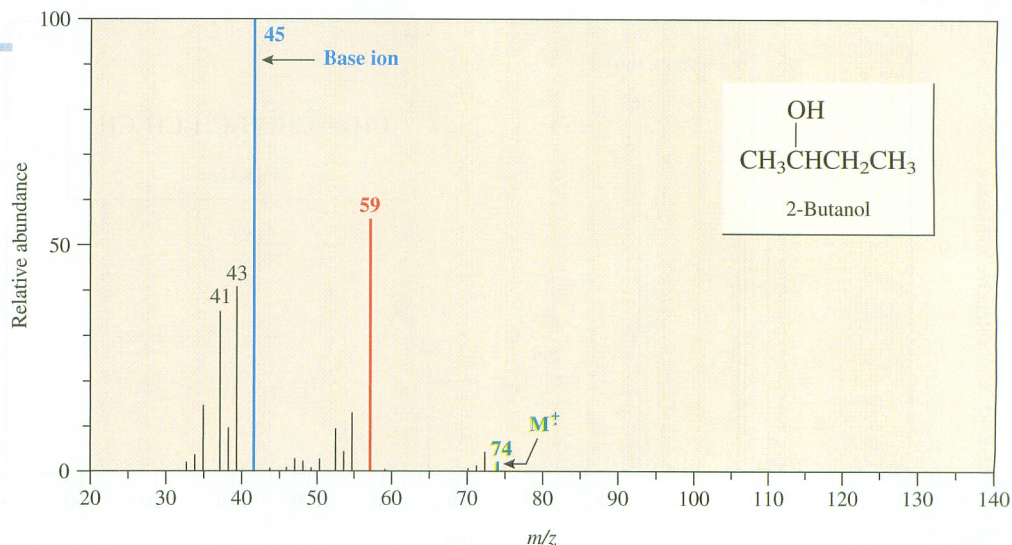
THE MASS SPECTRUM OF BUTYLBENZENE.

Alcohols

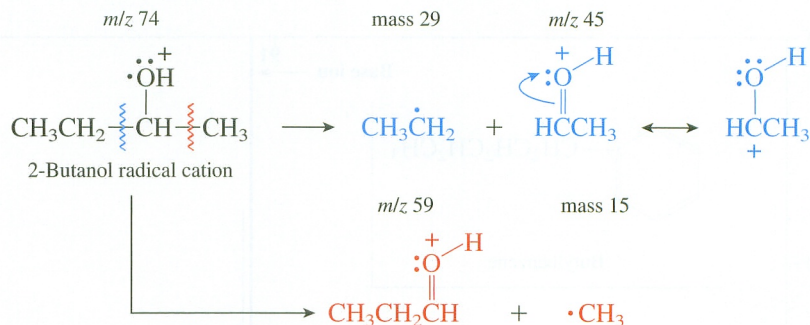
In addition to the elimination of water, alcohols tend to fragment by cleaving one of the bonds between the hydroxy carbon and an adjacent carbon. The resulting cations are the conjugate acids of aldehydes and ketones and are stabilized because they satisfy the octet rule at all of the atoms. Figure 15.12 shows the mass spectrum of 2-butanol.

Figure 15.12

THE MASS SPECTRUM OF 2-BUTANOL.

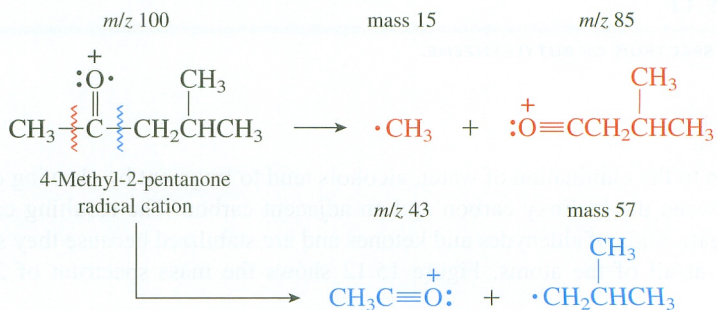


The major fragments for this alcohol, at m/z 59 and m/z 45, are formed by this type of fragmentation, as illustrated in the following equations:



Aldehydes and Ketones

A major fragmentation pathway in aldehydes and ketones is cleavage of the bonds to the carbonyl carbon. This process is similar to the fragmentation that occurs with alcohols and produces cations that are relatively stable because the octet rule is satisfied at all of the atoms. The major peaks at m/z 85 and m/z 43 in the spectrum of 4-methyl-2-pentanone (see Figure 15.13) result from this cleavage, as illustrated in the following equations:



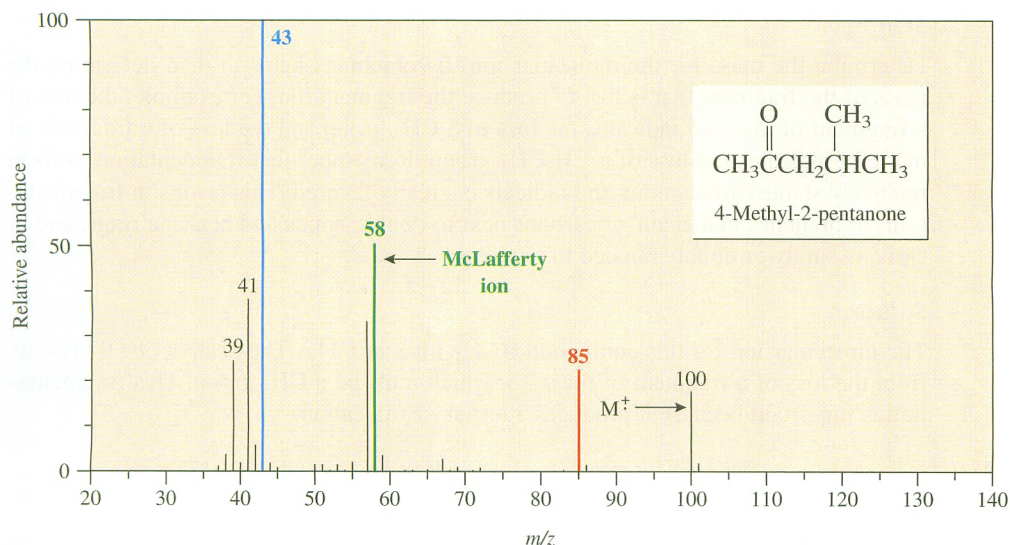
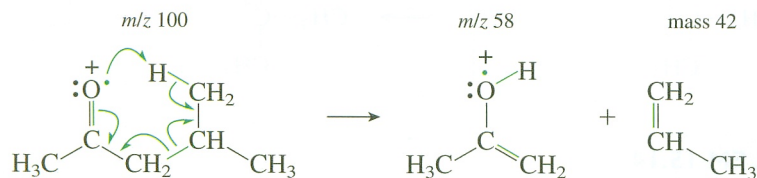


Figure 15.13

THE MASS SPECTRUM OF
4-METHYL-2-PENTANONE.

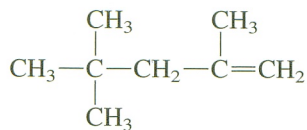
Aldehydes and ketones that have a hydrogen separated from the carbonyl carbon by three intervening carbons undergo a fragmentation called the McLafferty rearrangement. This process is illustrated in the following equation for 4-methyl-2-pentanone. It is responsible for the peak at m/z 58 in the mass spectrum shown in Figure 15.13. The McLafferty rearrangement is especially favorable because the cyclic transition state contains six atoms, a very favorable ring size.



These fragmentations serve to illustrate many of the major types. The driving force behind all of them is the formation of stable cations and radicals. Fragmentations of functional groups that have not been covered here are often similar to those described earlier. Although this has been only a very brief introduction to mass spectrometry, the power and utility of this technique should be apparent.

PRACTICE PROBLEM 15.2

Show equations to account for the major fragment ions that occur at m/z 97 and m/z 57 in the mass spectrum of 2,4,4-trimethyl-1-pentene.



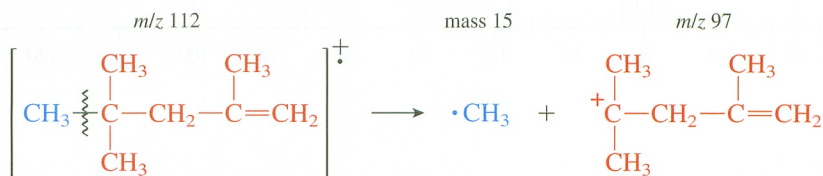
2,4,4-Trimethyl-1-pentene

Strategy

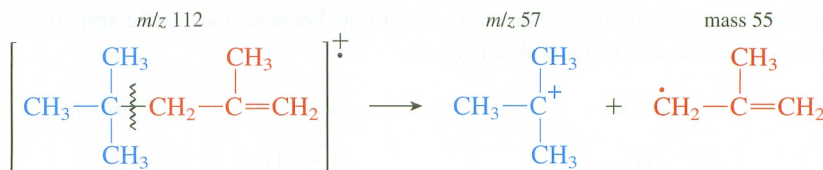
Determine the mass for the molecular ion. It sometimes helps to then determine the mass of the fragment that is lost to produce the fragment ion. For example, the loss of a fragment of mass 15 indicates the loss of a CH_3 group and the loss of a fragment of mass 29 indicates the loss of a CH_3CH_2 group. Remember that fragmentation to form relatively stable carbocations and radicals is greatly favored. This results in fragmentations at branches in a chain, at carbons next to double bonds and benzene rings, and at carbons singly or doubly bonded to oxygens.

Solution

The molecular ion for this compound (C_8H_{16}) has m/z 112. The peak at m/z 97 results from the loss of a fragment of mass 15, which must be a CH_3 group. This fragmentation is important because it produces a tertiary carbocation.



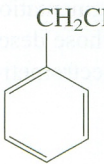
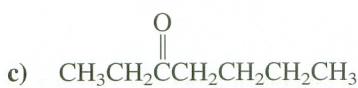
The peak at m/z 57 results from the fragmentation to produce a tertiary carbocation and an allylic radical according to the following equation. (As might be expected, the peak at m/z 57 is the base ion in the mass spectrum of this compound.)



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PROBLEM 15.14

Show equations to account for the major fragment ions that occur at the indicated m/z for these compounds:

- a)  m/z 91
- b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ m/z 31
- c)  m/z 85, 72, 57

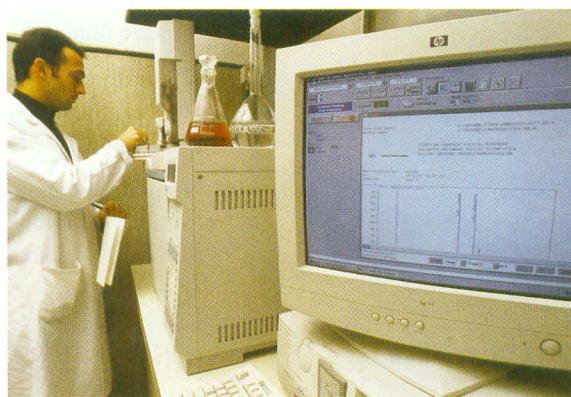
Focus On

Gas Chromatography and Mass Spectrometry

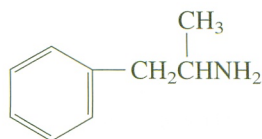
The techniques of gas chromatography (GC) and mass spectrometry (MS) have been combined into a powerful instrument, a GC/MS, for the identification of organic compounds. In this technique a small sample, containing a mixture of compounds, is injected onto the gas chromatograph, which separates the compounds. As the individual components elute from the column, they are passed directly into a mass spectrometer. The mass spectrum can be obtained without ever isolating the pure component.

Gas chromatography is an extremely powerful separation method. It requires only a very small amount of material and is able to separate even a complex mixture into its numerous components. The time that it takes for a particular compound to elute from the column under a given set of conditions, called the retention time, is characteristic for that compound. However, the identity of a component cannot be established solely on the basis of its retention time because another compound may coincidentally have an identical retention time. Whenever an analysis has a potential for legal or disciplinary consequences, the identity of the compound must be established by some other technique. Mass spectrometry is an ideal partner because it can establish the identity of a compound with certainty by using only the small amount of sample obtained from the GC.

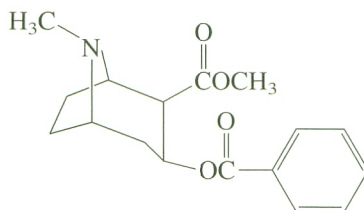
Extensive drug screening is done at many athletic events, such as the Olympic Games. Usually, separate analyses, using different extraction procedures, are done for stimulants, narcotics, anabolic steroids, diuretics, and peptide hormones. In the analysis for stimulants, which are amines such as amphetamine and cocaine, a 5 mL urine sample is first made basic with KOH to ensure that the amines are present as the neutral molecules rather than as salts. The free amines are then extracted from the sample with diethyl ether. To save time and expense, the sample is first analyzed by gas chromatography only. If a peak appears with the retention time of one of the proscribed stimulants, then the sample is reanalyzed by GC/MS to confirm the identity of the suspected compound.



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Amphetamine



Cocaine

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Review of Mastery Goals

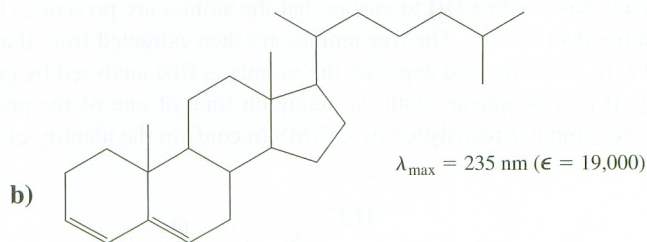
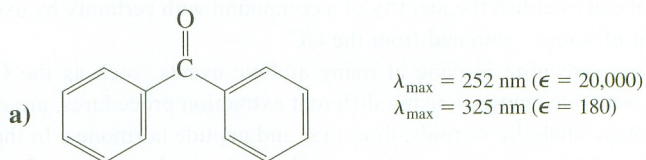
After completing this chapter, you should be able to:

- Determine whether a compound will absorb light in the ultraviolet or visible region. (Problems 15.17, 15.28, 15.29, and 15.30)
- Identify the chromophore and type of transition responsible for absorption of UV-visible radiation. (Problems 15.16 and 15.26)
- Determine whether sulfur, chlorine, bromine, or nitrogen is present in a compound by examination of the M , $M + 1$, and $M + 2$ peaks in its mass spectrum. (Problems 15.23 and 15.27)
- Explain the major fragmentation pathways for compounds containing some of the simple functional groups. (Problems 15.18, 15.19, 15.20, 15.21, 15.22, 15.23, 15.24, 15.25, and 15.31)

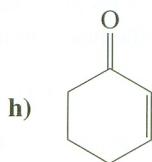
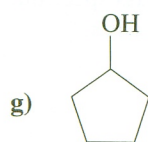
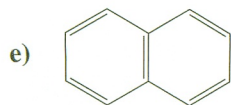
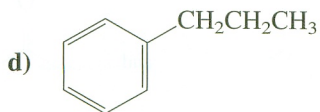
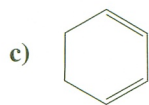
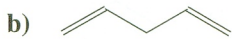
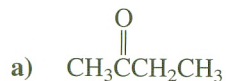
Additional Problems

15.15 A student wishes to record the UV spectrum of *trans*-stilbene, which has $\lambda_{\max} = 308 \text{ nm}$ ($\epsilon = 25,000$). What concentration should be prepared if the desired absorbance is 0.5 at the maximum?

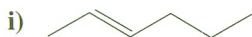
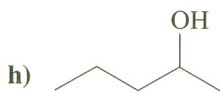
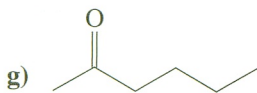
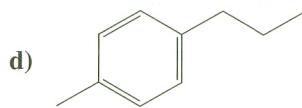
15.16 Indicate the types of transitions responsible for the absorptions of these compounds:



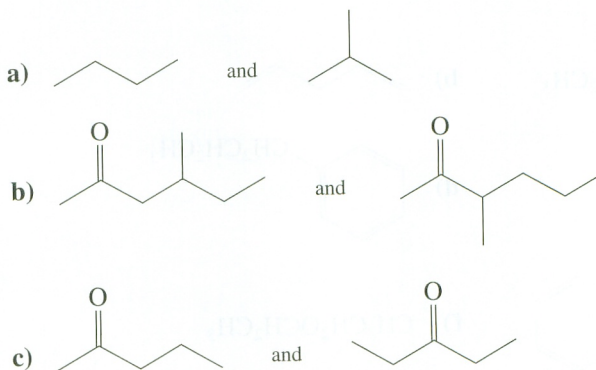
15.17 Which of these compounds are expected to have an absorption maximum in the region of 200 to 400 nm in their UV spectra?



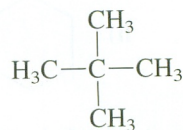
15.18 Predict the major fragments and their m/z that would appear in the mass spectra of these compounds:



15.19 Explain how mass spectrometry could be used to distinguish between these compounds:



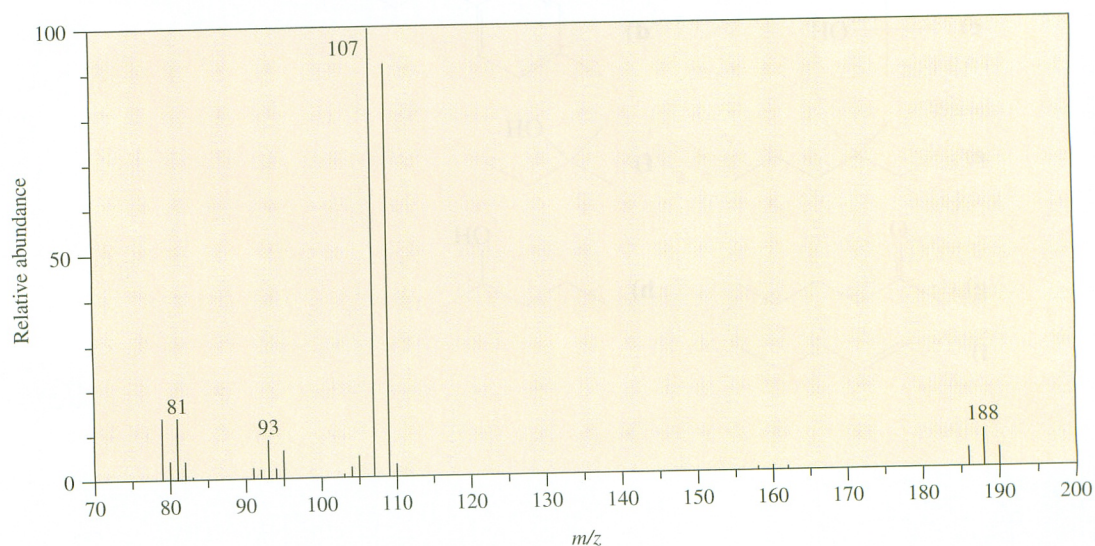
15.20 Explain why neopentane shows no molecular ion in its mass spectrum. Predict the structure and m/z for the base ion in its mass spectrum.



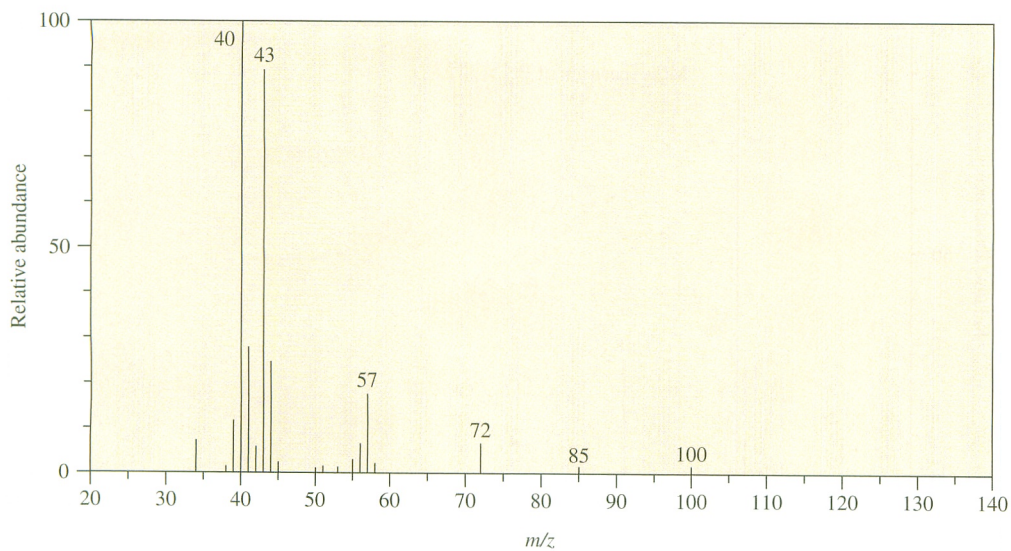
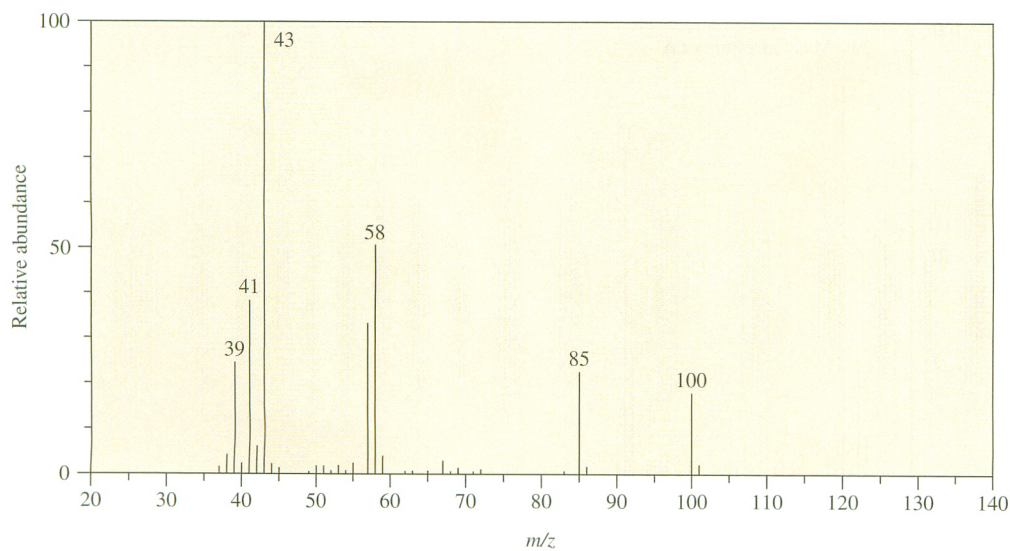
Neopentane

15.21 Explain how the peaks at m/z 115, 101, and 73 arise in the mass spectrum of 3-methyl-3-heptanol.

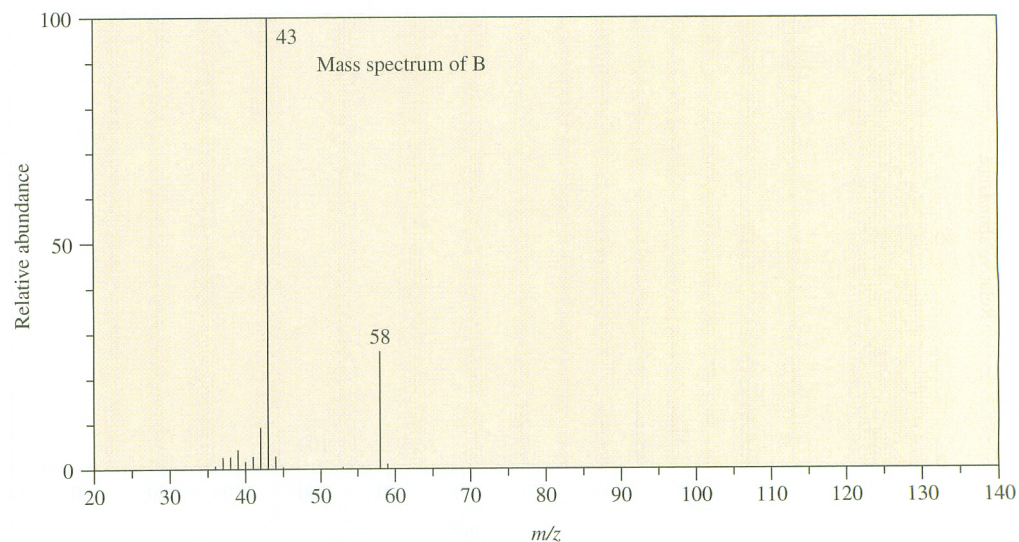
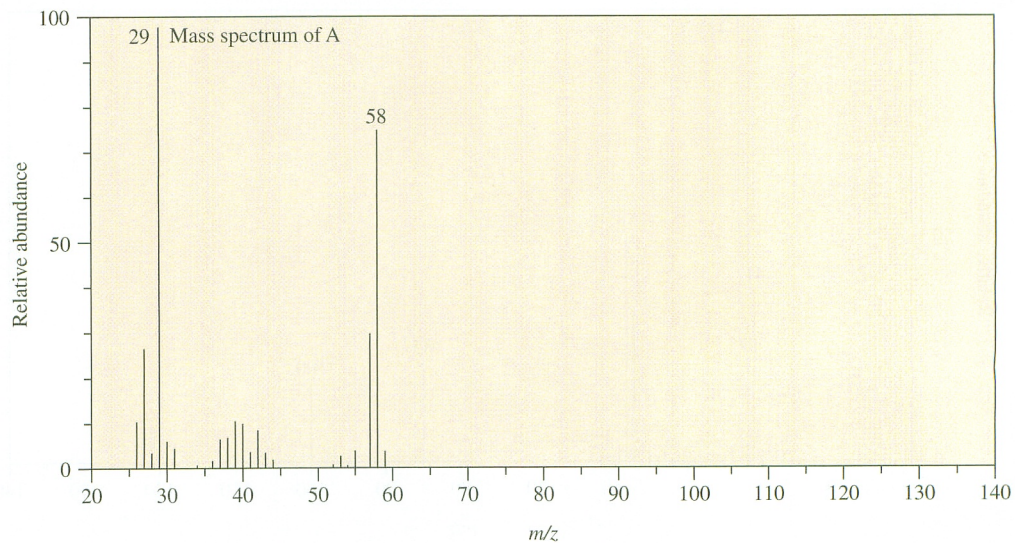
15.22 Suggest a structure for the compound whose mass spectrum is as follows:



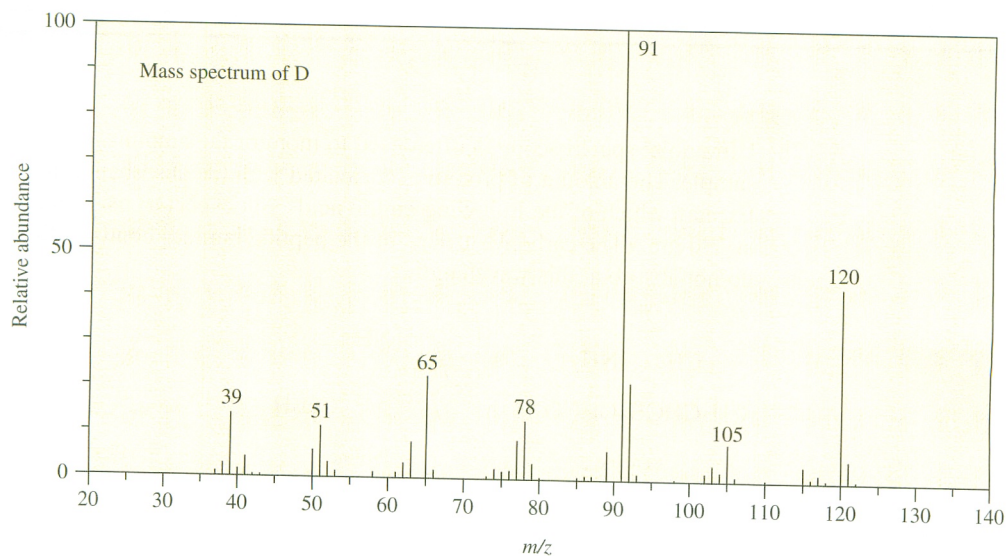
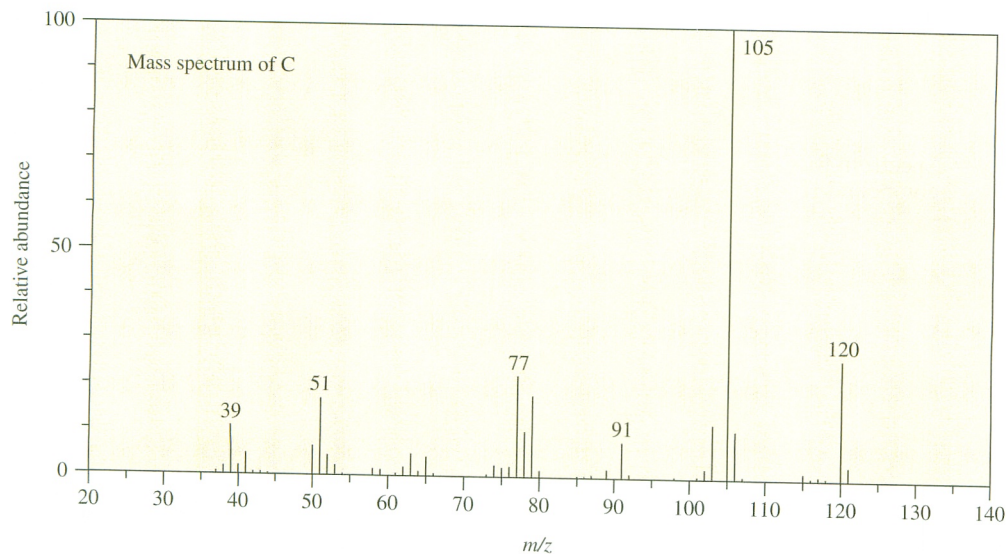
- 15.23** The mass spectra of 3-methyl-2-pentanone and 4-methyl-2-pentanone are as follows. Explain which spectrum goes with which compound. What is the structure of the ion responsible for the peak at m/z 43 in each spectrum?



15.24 Compounds **A** and **B** are isomers with the formula C_3H_6O . **A** has a peak at 1730 cm^{-1} in its IR spectrum and **B** has a peak at 1715 cm^{-1} . The mass spectra of **A** and **B** are as follows. Show the structures of **A** and **B**.

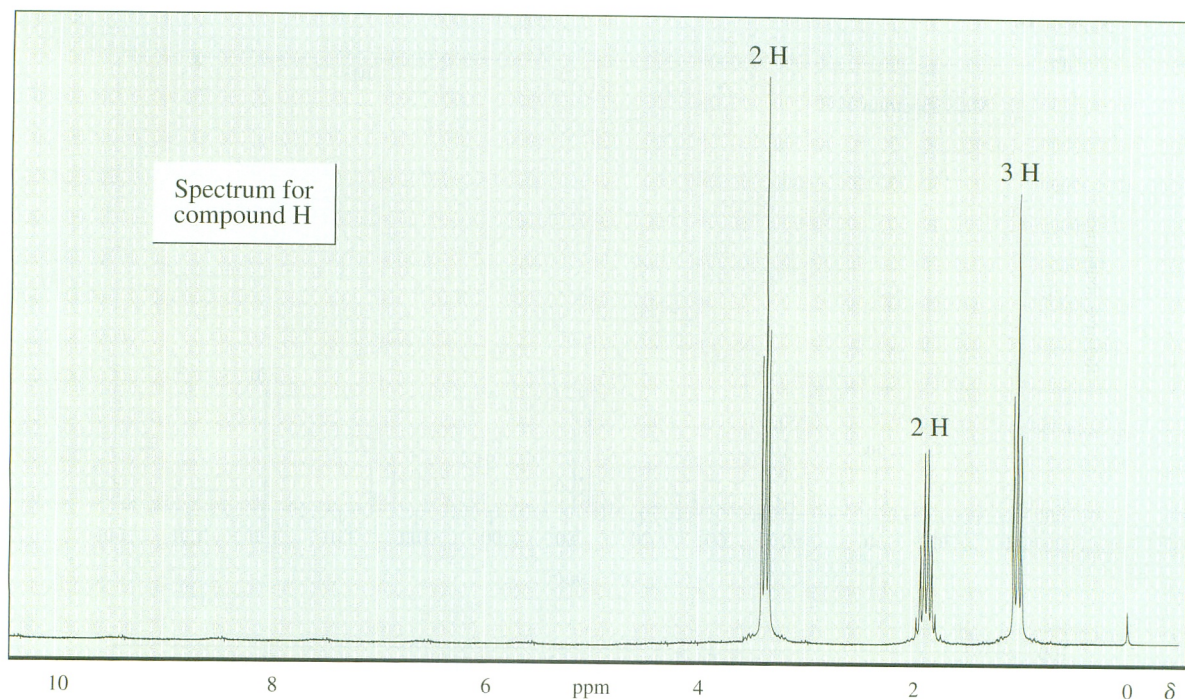


- 15.25** Compounds **C** and **D** are isomers with the formula C_9H_{12} . In addition to other absorption peaks, both compounds show a peak near 7.25δ (area 5) in their 1H -NMR spectra. Their mass spectra are as follows. Show the structures of **C** and **D**.

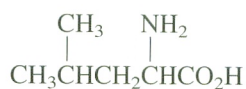


- 15.26** Compounds **E** and **F** are isomers with the formula C_6H_8 . Both react with H_2 in the presence of Pt to give **G** (C_6H_{12}). **G** shows a single peak in its ^{13}C -NMR spectrum. **E** has no absorption maximum above 200 nm in its UV spectrum, whereas **F** has $\lambda_{max} = 259 \text{ nm}$ ($\epsilon = 10,000$). Show the structures of **E**, **F**, and **G**.

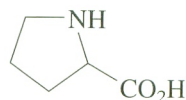
- 15.27** The ^1H -NMR spectrum for compound **H** is as follows. The peaks at highest m/z in the mass spectrum of **H** appear at 122 and 124 with intensities in a ratio of about 1 to 1. Show the structure of **H**.



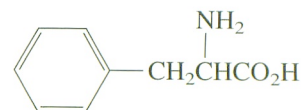
- 15.28** Ultraviolet spectroscopy is often used to monitor the amount of a protein in a sample. The amount of protein is correlated with the absorbance at 280 nm. Explain which of the following amino acids you expect to have an absorption at 280 nm. (The carbonyl groups of the peptide [amide] bonds of the protein do not absorb at this wavelength.)



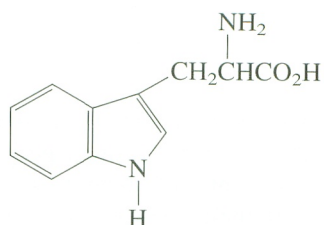
Leucine



Proline



Phenylalanine



Tryptophan



Serine

Problems Using Online Three-Dimensional Molecular Models

- 15.29** Explain why the ultraviolet spectrum of one of these dienes has its maximum absorption at a longer wavelength than that of the other.
- 15.30** Explain why the ultraviolet spectrum of one of these compounds has its maximum absorption at a longer wavelength than that of the other.
- 15.31** Show the structures of the fragment ions that occur at m/z 57, 86, and 99 in the mass spectrum of this compound.

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